BASE HYDROLYSIS REACTION OF DICHLOROETHOXYOXO-BIS(TRIPHENYLPHOSPHINE)RHENIUM(V)
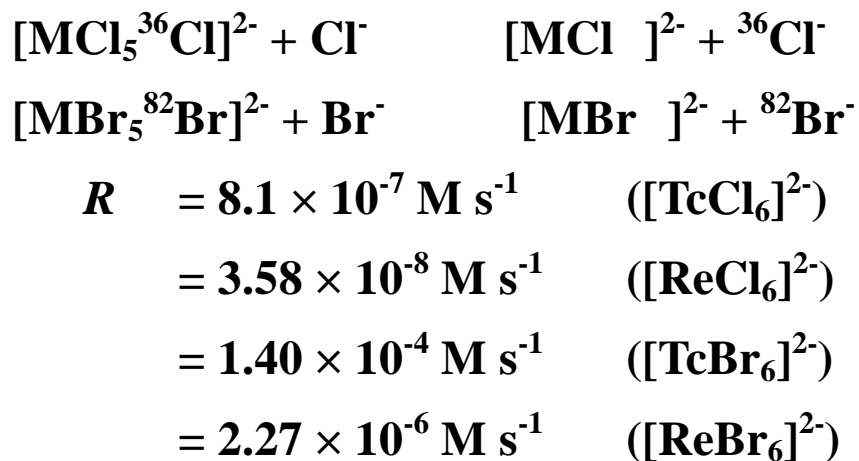
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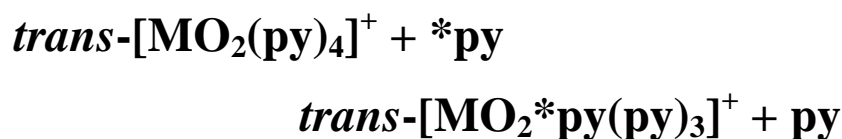
Inertness of Re complexes

1. **Tc(IV) and Re(IV) complexes**

   $$[MCl_5{}^{36}Cl]^{2-} + Cl^- \qquad [MCl_6]^{2-} + {}^{36}Cl^-$$

   $$[MBr_5{}^{82}Br]^{2-} + Br^- \qquad [MBr_6]^{2-} + {}^{82}Br^-$$

   $$R \quad = 8.1 \times 10^{-7} \text{ M s}^{-1} \qquad ([TcCl_6]^{2-})$$
   $$= 3.58 \times 10^{-8} \text{ M s}^{-1} \qquad ([ReCl_6]^{2-})$$
   $$= 1.40 \times 10^{-4} \text{ M s}^{-1} \qquad ([TcBr_6]^{2-})$$
   $$= 2.27 \times 10^{-6} \text{ M s}^{-1} \qquad ([ReBr_6]^{2-})$$

   K. Schwochau (1965)

2. **Tc(V) and Re(V) complexes**

   trans-$[MO_2(py)_4]^+$ + *py

   $$\textit{trans-}[MO_2{*}py(py)_3]^+ + py$$

   k_{Tc}/k_{Re} **8000 (298 K)**

   L. Helm *et al*. (1992)

   cf. $[MO(DBDS)]^-$ + $H_2{}^{17}O$

   $$[M^{17}O(DBDS)]^- + H_2O$$

   $R = k[MO(DBDS)^-][CH_3O^-]$

   k_{Tc}/k_{Re} **0.1**

   DBDS: *N,N'*-bis(mercaptoacetyl)butane-1,4-diamine

   B. Chen *et al*. (1992)

Hydrolysis of $[Re(tu)_6]^{3+}$

$$[Re(tu)_6]^{3+} + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Re(H_2O)(tu)_5]^{3+} + tu$$

$$\overset{k_3}{\longrightarrow} \text{ decomposition products}$$
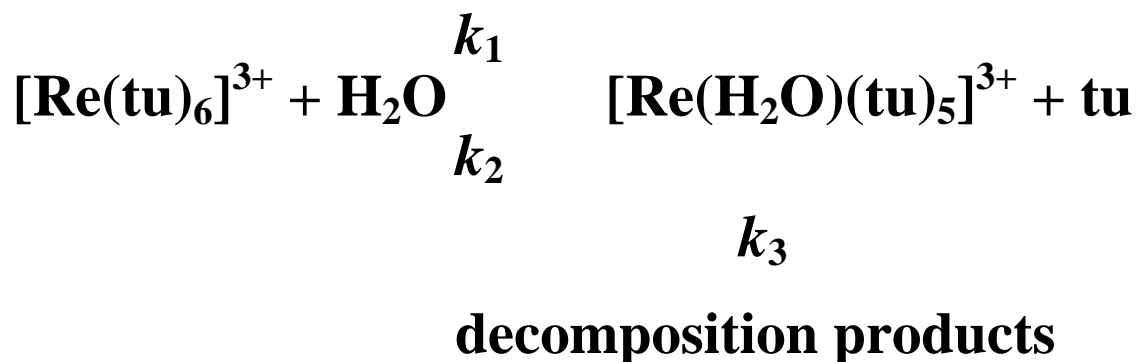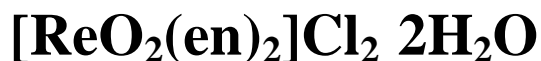
$$k_{app} = \frac{k_1 k_3}{k_2[tu] + k_1}$$

$$k_1 = 8.4 \times 10^{-3} \text{ s}^{-1}$$

$$k_2 = 2.7 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$$

$$k_3 = 2.0 \times 10^{-4} \text{ s}^{-1} \qquad \text{at } 25$$

tu: thiourea

Syntheses of Re(IV) and Re(V) complexes using dichloroethoxyoxobis(triphenylphos-phine)rhenium(V) ([ReOCl$_2$(OEt)(PPh$_3$)$_2$]) as a starting complex

[ReO$_2$(en)$_2$]Cl$_2$ 2H$_2$O

N. P. Johnson et al. (1964)

[ReX$_2$(acac)$_2$(PPh$_3$)$_2$]   (X=Cl, Br)

D. E. Grove et al. (1965)

Experimental

1. Synthesis of [ReOCl$_2$(OEt)(PPh$_3$)$_2$]

NH$_4$ReO$_4$ in concd. HCl

$+$ **hot EtOH**

$+$ **PPh$_3$ in a hot EtOH soln.**

ppt   **soln.**

**Recrystallization from
benzene-petroleum ether**

2. Kinetic runs

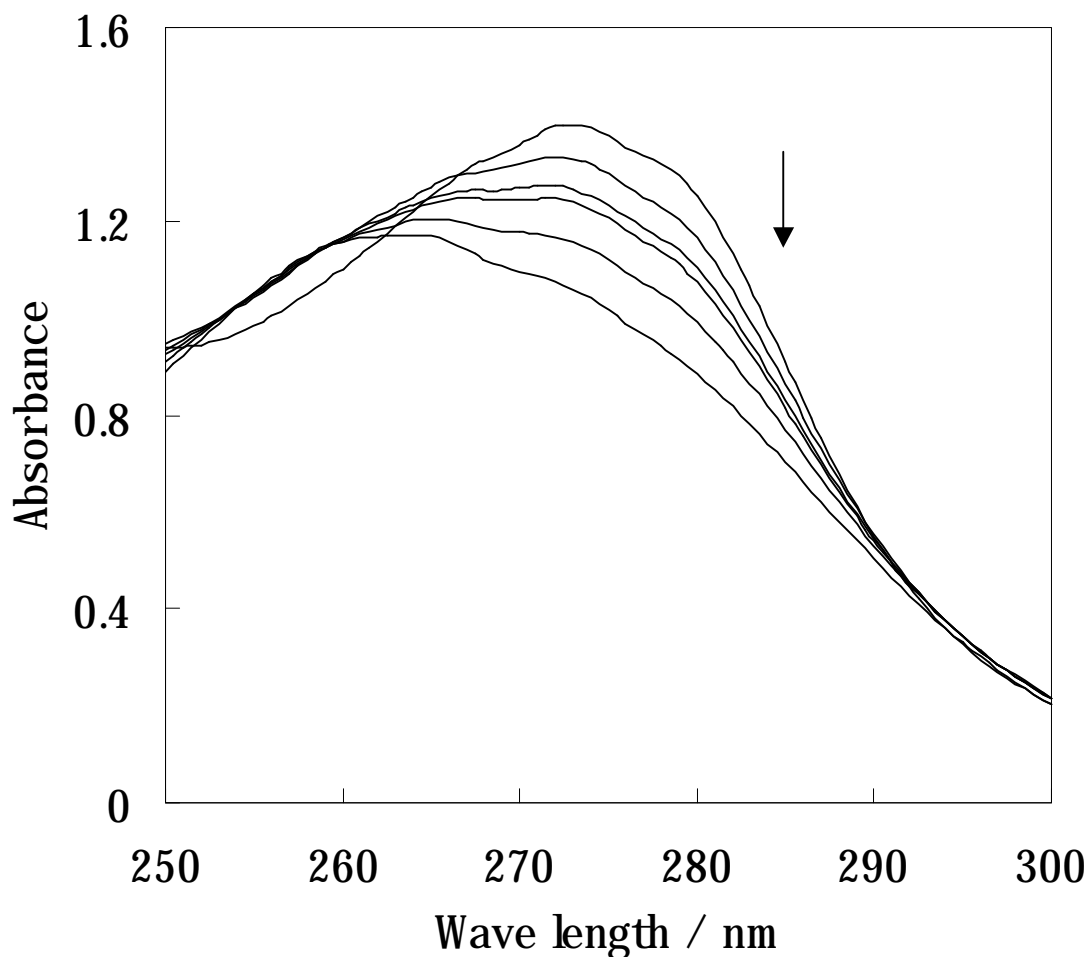**[ReOCl$_2$(OEt)(PPh$_3$)$_2$] in CHCl$_3$**

$+$ **NaOH**

Shaking at 25

org.   **aq.**

**Measurement of
the absorbance
at 273 nm**

Fig. Variation of the absorption spectra of [ReOCl$_2$(OEt)(PPh$_3$)$_2$] in CHCl$_3$ solution

Aqueous phase: 1 M NaOH solution

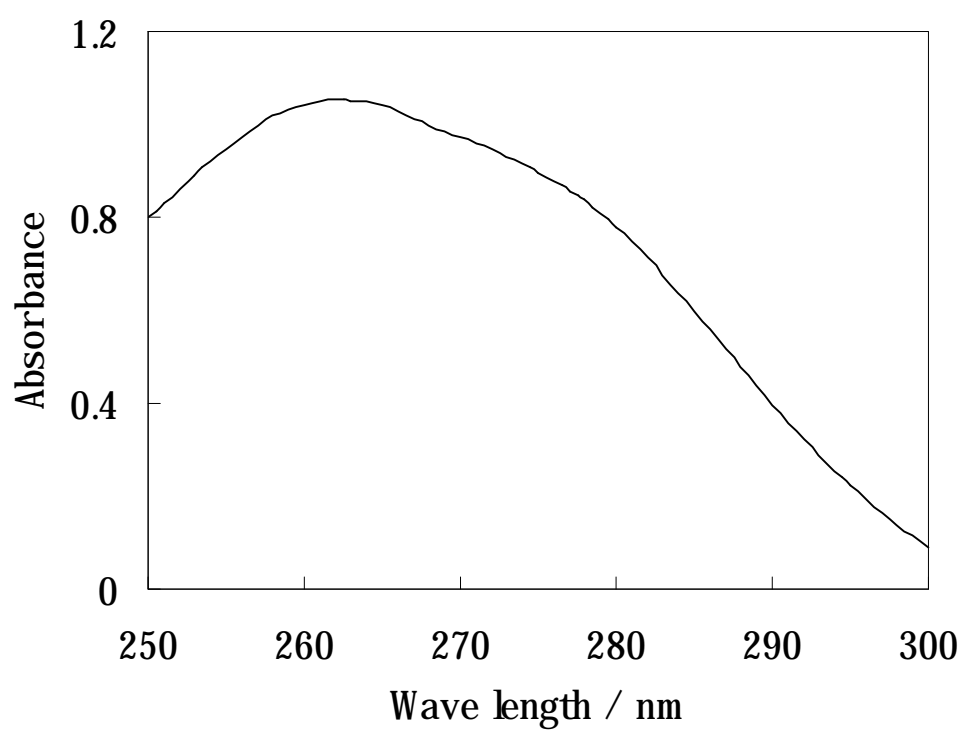Fig.　Absorption spectrum of triphenylphosphine in CHCl₃

$[\text{OH}^-]$ $[\text{C}]_0$

$$-\frac{d[\text{C}]}{dt} = k_{\text{app}}[\text{C}]$$

$$[\text{C}]_t = [\text{C}]_0 \exp(-k_{\text{app}}t)$$

$$\ln\frac{[\text{C}]_t}{[\text{C}]_0} = -k_{\text{app}}t$$

C: $[\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2]$

A: absorbance of $[ReOCl_2(OEt)(PPh_3)_2]$ in the organic phase at 273 nm

$\mathring{a}_c$: molar absorption coefficient of $[ReOCl_2(OEt)(PPh_3)_2]$

$\mathring{a}_p$: molar absorption coefficient of PPh_3 (P)

$$A_0 = \mathring{a}_c[C]_0$$

$$A_\infty = \mathring{a}_p[P]_\infty = 2\mathring{a}_p[C]_0$$

$$A_t = \mathring{a}_c[C]_t + \mathring{a}_p[P]_t$$

$$= \mathring{a}_c[C]_t + 2\mathring{a}_p([C]_0 - [C]_t)$$

$$= (\mathring{a}_c - 2\mathring{a}_p)[C]_t + 2\mathring{a}_p[C]_0$$

$$\frac{[C]_t}{[C]_0} = \frac{A_t - A_\infty}{A_0 - A_\infty}$$

$$\ln\frac{(A_t - A_\infty)}{(A_0 - A_\infty)} = -k_{app}t$$

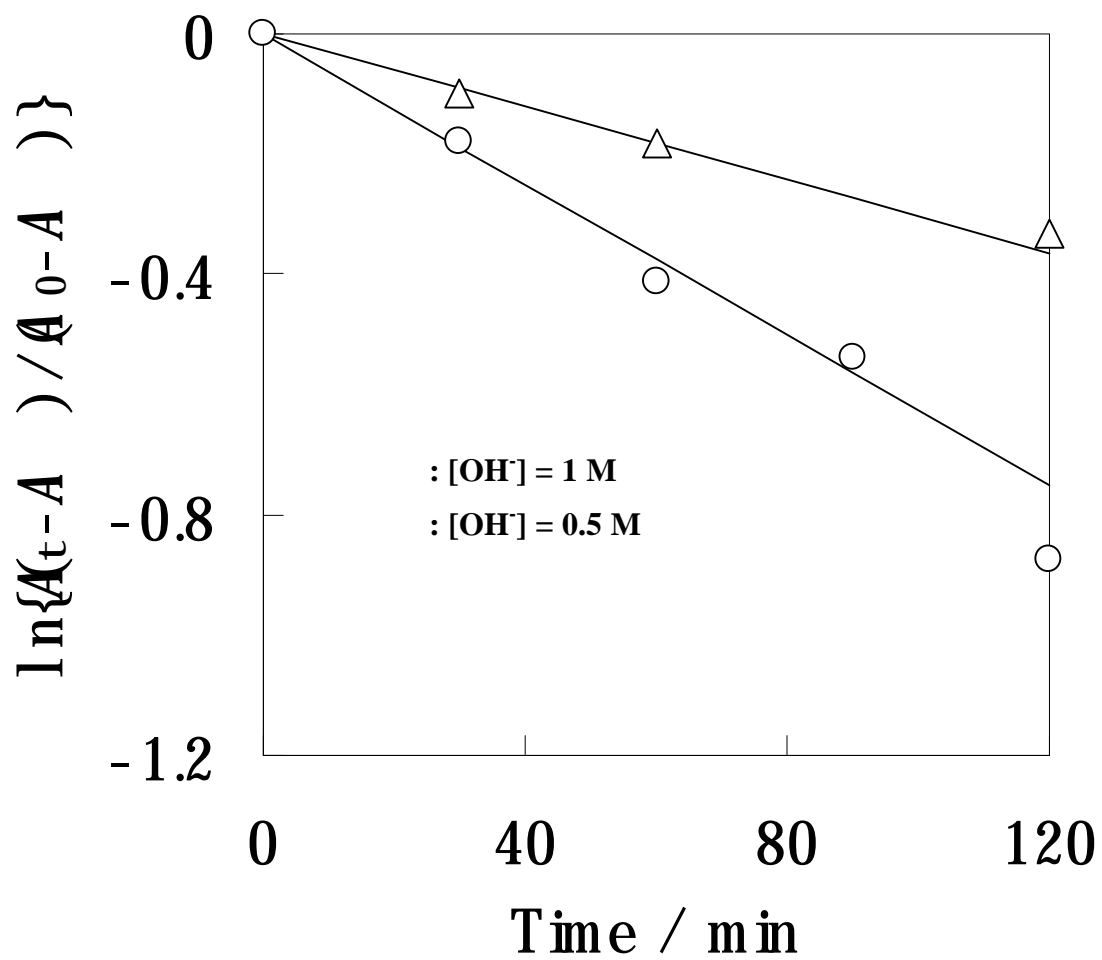Fig. $\ln\{(A_t - A_\infty)/(A_0 - A_\infty)\}$ vs. time
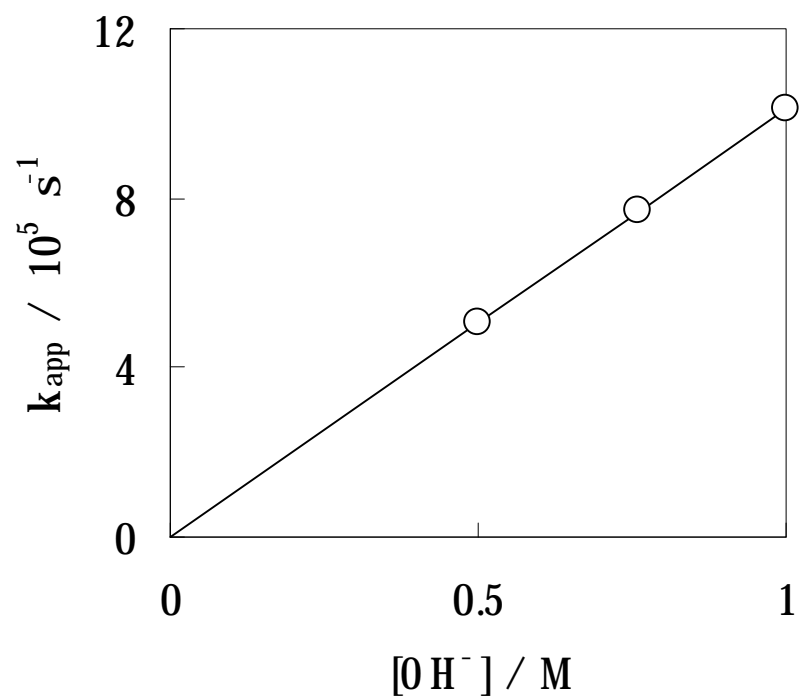
Fig. k_{app} vs. [OH⁻]

Table   Apparent Rate Constant k_{app}
(25   )

[OH⁻] / M	k_{app} / s⁻¹
0.50	5.1×10^{-5}
0.76	7.6×10^{-5}
1.0	1.0×10^{-4}

$k_{app} = k \, [OH^-]$

$k = 1.03 \times 10^{-4} \, M^{-1}s^{-1}$ (25   )

Base Hydrolysis Reactions of Tc complexes

1. $R = k[\text{OH}^-][\text{C}]$

   cis-[TcOCl(acac)$_2$]

   cis-[TcOCl(bzac)$_2$]

2. $R = (k_1[\text{OH}^-] + \dfrac{k_2 k_4[\text{OH}^-]}{k_3[\text{Cl}^-] + k_4[\text{OH}^-]})[\text{C}]$

   cis-[TcOCl(dbm)$_2$]

   cis-[TcOCl(ox)$_2$]

   cis-[TcOBr(ox)$_2$]

   cis-[TcCl$_2$(acac)$_2$]

   cis-[TcBr$_2$(acac)$_2$]

3. $R = (k_1[\text{OH}^-] + k_2[\text{OH}^-]^2)[\text{C}]$

   [Tc(acac)$_3$]

4.

$$\frac{A_\infty - A_t}{A_\infty - A_0} = \exp(-k_1 t) + \frac{k_1}{k_1 - k'_2}(\mathbf{e}_B - \mathbf{e}_{acac})$$
$$\times \{\exp(-k'_2) - \exp(-k_1 t)\}$$

$$k'_2 = k_2[\text{OH}^-]$$

   [TcN(acac)$_2$]

Table   Rate constant for $R = k[\text{OH}^-][\text{C}]$

Complex	k / $\text{M}^{-1}\text{s}^{-1}$ (25)
[TcN(acac)$_2$]	8.2×10^{-4}
cis-[TcCl$_2$(acac)$_2$]	1.5×10^{-4}
[ReOCl$_2$(OEt)(PPh$_3$)$_2$]	**1.0×10^{-4}**
cis-[TcBr$_2$(acac)$_2$]	1.0×10^{-4}
cis-[TcOCl(bzac)$_2$]	1.3×10^{-5}
cis-[TcOCl(acac)$_2$]	1.0×10^{-5}
cis-[TcOCl(ox)$_2$]	4.4×10^{-6}
cis-[TcOBr(ox)$_2$]	2.4×10^{-6}
cis-[TcOCl(dbm)$_2$]	3.3×10^{-7}
[Tc(acac)$_3$]	3.3×10^{-5} (35.5)